

# Mn L<sub>2,3</sub> and O K XANES Spectroscopy of Mn Mineral Surfaces

G.A. Waychunas<sup>1</sup>, D.K. Shuh<sup>2</sup>, D.A. Shaughnessey<sup>2</sup> and H. Nitsche<sup>2,3</sup>

<sup>1</sup>Earth Science Division, E.O. Lawrence Berkeley National Laboratory

<sup>2</sup>Chemical Sciences Division and Glenn T. Seaborg Center, E.O. Lawrence Berkeley National Laboratory

<sup>3</sup>Department of Chemistry

University of California, Berkeley, California 94720

## INTRODUCTION

Mn oxyhydroxides are now known to be important in the natural sequestration and redox reactions with toxic metals and actinides, despite their usual small volume in natural soils, sediments and rock units [1,2]. Mn oxyhydroxides are also important products of cell metabolism, and Mn complexes serve as electron transfer sites in plant and animal tissues to promote energy transfer. Coupled to our work with Ca compounds, we are developing methodology to determine the valence of surface Mn and reactant species on Mn oxyhydroxide single crystals. This effort consists of K edge (1s) spectroscopy at SSRL utilizing grazing incidence methods, and L<sub>2,3</sub> edge (2p) spectroscopy at the ALS both under dry UHV conditions and in contact with aqueous solutions, to measure surface speciation both of reactant and substrate. Our ALS work reported here demonstrates the utility of L<sub>2,3</sub> spectra in determining Mn valence state, and of O K spectra in identifying d character and O-metal coordination environment. Together with measurements of surface solution reactions via grazing incidence Mn K edge spectroscopy, the complete picture of aqueous interfacial redox reactions can be characterized.

## RESULTS

Figure 1 shows Mn L<sub>2,3</sub> XANES from a set of Mn oxyhydroxides, obtained under UHV conditions on beamline 9.3.2. It is clear that the different valence states of Mn give rise to distinct spectral signatures that change little in going from one structure type to another. This is so because in most Mn oxyhydroxides Mn resides in an octahedral site coordinated by oxygen, so that differences in 3d crystal field levels between structures is small [3]. Hence cryptomelane and ramsdellite, the former having the hollandite structure and the latter the goethite structure, both show nearly identical Mn<sup>4+</sup> features. Manganite, MnOOH, was studied as a cleaved single crystal, as a natural single crystal, and as reagent powder. Clearly the surface of the natural crystal is dominated by Mn<sup>4+</sup> with minor Mn<sup>3+</sup>, while the cleaved crystal shows only Mn<sup>3+</sup>. Bixbyite, a solid solution of Fe<sub>2</sub>O<sub>3</sub> and Mn<sub>2</sub>O<sub>3</sub> with an anion-deficient fluorite structure, shows only Mn<sup>3+</sup> at the surface of a polished single crystal. Hausmannite, a distorted spinel structure with both Mn<sup>2+</sup> and Mn<sup>3+</sup> shows addition of a few sharp Mn<sup>2+</sup> spectral features. Besides the

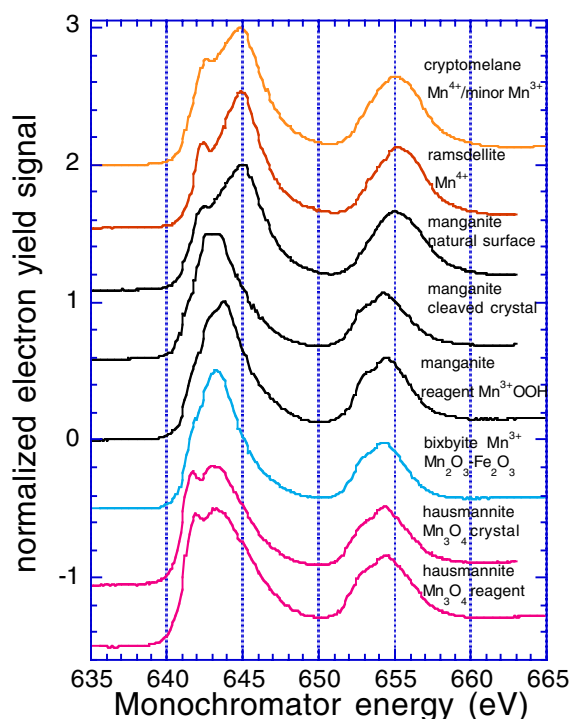


Fig.1 Mn L<sub>2,3</sub> XANES for Mn oxyhydroxides.

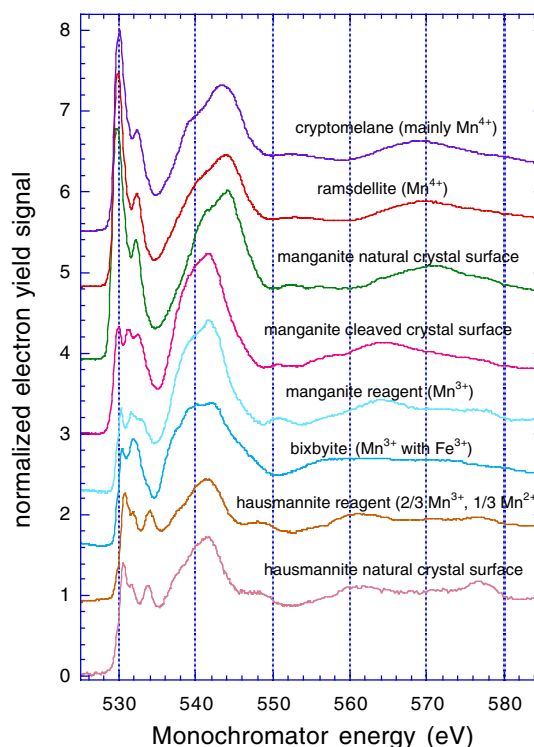


Fig.2 O K XANES for Mn oxyhydroxides.

Both series of spectra collected with total electron yield on ALS beamline 9.3.2

specific edge differences, there is also a valence-related energy shift of the edge of about 1 eV/valence unit. Figure 2 shows the O K edge XANES (and lower energy EXAFS) for the same samples. The effect of surface oxidation on manganite single crystals is clearly shown by the much different O K edge in the cleaved sample. We find that O K spectra mainly represent structural differences among the various Mn oxyhydroxides, rather than being sensitive to Mn valence alone. This is shown by the differences in the bixbyite and manganite (cleaved or reagent) spectra. There is also a dramatic difference in the 3d bands in the energy range from 529 to 535 eV as a function of valence. In part, this reflects the decreased 3d occupancy in going from Mn<sup>2+</sup> to Mn<sup>4+</sup>, which intensifies these features, and in part differences in 2p-3d orbital mixing. These features can be evaluated with present ab initio quantum codes, and this work is in progress [4,5].

We have also recently recorded additional spectra of Mn-minerals birnessite, rhodocrosite, spessartite, rhodonite, and a suite of Mn-doped minerals and are evaluating the surface reactivity

of Mn in single crystals as a function of structure and valence state. We will be acquiring Mn L edge spectra under hydrous conditions at the ALS in the near future, along with grazing incidence and standing wave K edge studies at SSRL, and will extend work to the mineral-solution interface. We are also evaluating the effects of radiation dose on Mn valence state. This is expected to be a problem mainly in Mn-doped insulating materials and Mn oxide nanocrystals. For example, Mn doped natural tourmaline (a borosilicate) shows a valence ratio depending on dosage due to natural radioactivity [6].

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Principal investigator: Glenn Waychunas, Earth Sciences Division, E. O. Lawrence Berkeley National Laboratory.  
Email: gawaychunas@lbl.gov. Telephone: 510-495-2224.